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# SPECIFICATION

Electronic Version 1.2.8

Stylesheet Version 1.0

## NON-PLASMA REACTION APPARATUS AND METHOD

### Background of the Invention

[0001] Technical Field

[0002] The present invention generally relates to an apparatus and method for forming a surface film, and more particularly, to an apparatus and method for performing a non-plasma chemical reaction to form the surface film.

[0003] Background Art

[0004] The ability to control etching by hydrogen fluoride (HF) to a given thickness of a surface layer of a workpiece that has been adapted for etching is an important prerequisite for accurate etching in the manufacture of an integrated circuit (IC). The surface layer of the workpiece may be adapted for etching by forming a surface layer that is an oxide of the material of the workpiece. If the workpiece comprises silicon or germanium, the surface layer of the workpiece may be adapted for etching by forming the surface layer of silicon dioxide ( $\text{SiO}_2$ ) or germanium dioxide ( $\text{GeO}_2$ ). Pure hydrogen fluoride (HF) may etch the adapted surface layer by forming gaseous silicon tetrafluoride ( $\text{SiF}_4$ ). The gaseous  $\text{SiF}_4$  is very volatile such that exposing the surface layer to HF readily etches the surface layer, thereby exposing a remaining layer of oxide to etching by the HF. Etching to the given thickness is difficult to control because the formation of  $\text{SiF}_4$  continues until the surface layer, i.e., the oxide layer, has been completely etched due to formation and evaporation of  $\text{SiF}_4$ .

[0005] In view of the need to control the etching thickness when the adapted surface layer of a workpiece is exposed to HF, there is a need for an apparatus and method that provides controlled etching of the adapted surface layer with HF.

## Brief Summary of the Invention

- [0006] The present invention provides an apparatus for forming a self-limiting etchable layer on a workpiece, comprising:
- [0007] a chamber adapted for holding a workpiece, wherein a surface layer of the workpiece has been adapted for being etched; and
- [0008] a distribution plate within the chamber, wherein the distribution plate comprises a first plurality of channels for providing a first fluid to flow into the chamber at an angle  $\theta_1$  with respect to an exposed surface of the distribution plate and a second plurality of channels for providing a second fluid to flow into the chamber at an angle  $\theta_2$  with respect to the exposed surface of the distribution plate, and wherein the first plurality of channels and the second plurality of channels are arranged in rings around a common point of the distribution plate;
- [0009] wherein the first fluid and the second fluid are adapted to react inside the chamber to form a self-limiting etchable layer on a portion of the adapted surface layer of the workpiece.
- [0010] A second embodiment of the present invention provides a method comprising:
- [0011] providing a workpiece within a chamber, wherein a surface layer of the workpiece has been adapted for being etched;
- [0012] providing a distribution plate over the workpiece, wherein the distribution plate includes a first plurality of channels for providing a first fluid to flow into the chamber at an angle  $\theta_1$  with respect to an exposed surface of the distribution plate and a second plurality of channels for providing a second fluid to flow into the chamber at an angle  $\theta_2$  with respect to the exposed surface of the distribution plate, and wherein the first plurality of channels and the second plurality of channels are arranged in rings around a common point of the distribution plate; and
- [0013] forming a self-limiting etchable layer by providing the first and second fluids over the adapted surface layer of the workpiece.
- [0014] A third embodiment of the present invention provides a distribution plate

comprising:

- [0015] a first plurality of channels for providing a first fluid to flow into a chamber at an angle  $\theta_1$  with respect to an exposed surface of the distribution plate; and
- [0016] a second plurality of channels for providing a second fluid to flow into the chamber at an angle  $\theta_2$  with respect to the exposed surface of the distribution plate;
- [0017] wherein the first plurality of channels and the second plurality of channels are arranged in rings around a common point of the distribution plate.

### Brief Description of the Several Views of the Drawings

- [0018] FIG. 1 depicts an exterior view of a single-substrate-processing non-plasma reaction apparatus, according to embodiments of the present invention;
- [0019] FIG. 2 depicts a top interior view of FIG. 1 after opening a lid of the apparatus and rotating it in a counter-clockwise direction on a longitudinal axis through a center of the apparatus;
- [0020] FIG. 3 depicts a top view of an electrostatic chuck of the apparatus;
- [0021] FIG. 4 depicts a longitudinal cross-sectional view taken along line 4-4 of FIG. 1;
- [0022] FIG. 5 depicts a cross-sectional view taken along line 5-5 of FIG. 4 of a center portion of a distribution plate;
- [0023] FIG. 6A depicts a cross-sectional view taken along line 6-6 of FIG. 4 of a portion of the distribution plate;
- [0024] FIG. 6B depicts FIG. 6A, wherein three dimensional XYZ axes are superimposed on the cross-sectional view depicted by FIG. 6A, taken along line 6-6 of FIG. 4; FIG. 7 depicts an exploded frontal interior view of the apparatus; and
- [0025] FIG. 8 depicts a method for forming a self-limiting etchable layer, according to embodiments of the present invention.

### Detailed Description of the Invention

- [0026] The present invention discloses an apparatus and method that provides controlled

etching of an adapted surface layer of a workpiece or wafer by reaction of the adapted surface layer with ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ), forming a self-limiting etchable layer, ammonium hexafluorosilicate, ( $\text{NH}_4$ )<sub>2</sub>SiF<sub>6</sub>, that may be removed by thermal desorption.  $\text{NH}_5\text{F}_2$  may be formed by mixing a first fluid, ammonia ( $\text{NH}_3$ ) and a second fluid, hydrogen fluoride (HF). The adapted surface layer on the workpiece may comprise an oxide layer, formed by thermal oxidation or tetraethoxysilane (TEOS) oxidation of a portion of the surface of the workpiece or wafer. Etching the adapted surface layer with HF alone to a given thickness is difficult to control because the formation of SiF<sub>4</sub> continues until the surface layer, i.e., the oxide layer, has been completely etched due to formation and evaporation of SiF<sub>4</sub>. Reaction of the adapted surface layer with ( $\text{NH}_5\text{F}_2$ ) forms the self-limiting etchable layer, ( $\text{NH}_4$ )<sub>2</sub>SiF<sub>6</sub>, that provides controlled etching of an adapted surface layer of a workpiece or wafer because the self-limiting layer has reduced permeability to HF in the  $\text{NH}_3$  and HF mixture.

[0027] Jeng et al. disclose in commonly assigned U.S. Patent No. 5,282,925, herein incorporated by reference, a method for formation of a self-limiting etchable layer. Hereinafter, a self-limiting etchable layer includes layers made of materials such as ammonium hexafluorosilicate, ( $\text{NH}_4$ )<sub>2</sub>SiF<sub>6</sub>, that may become impervious to continued exposure to hydrogen fluoride (HF), resulting in an ability to control an etching thickness. In Jeng et al., a surface layer of a silicon wafer is adapted to being etched by forming an oxide layer such as a silicon dioxide (SiO<sub>2</sub>) layer on the surface of the wafer. In Jeng et al., a portion of the SiO<sub>2</sub> layer becomes a self-limiting etchable layer when the portion of the layer of SiO<sub>2</sub> undergoes a non-plasma reaction with ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ), producing the self-limiting etchable layer of ( $\text{NH}_4$ )<sub>2</sub>SiF<sub>6</sub> and a remaining layer of unreacted SiO<sub>2</sub>. According to Jeng et al.,  $\text{NH}_5\text{F}_2$  may be produced by chemical combination of two (2) moles of HF and one (1) mole of ammonia ( $\text{NH}_3$ ). Hereinafter, "providing a stoichiometric number of moles of HF to  $\text{NH}_3$  needed to form ammonium bifluoride ( $\text{NH}_5\text{F}_2$ )" or "providing a stoichiometric molar ratio of HF: $\text{NH}_3$  = 2 needed to form  $\text{NH}_5\text{F}_2$ " means providing two (2) moles of HF and one (1) mole of ammonia ( $\text{NH}_3$ ) to form  $\text{NH}_5\text{F}_2$ .

[0028] Pure hydrogen fluoride (HF) may etch the adapted surface layer by forming gaseous silicon tetrafluoride (SiF<sub>4</sub>). The gaseous SiF<sub>4</sub> is very volatile such that

exposing the surface layer to HF readily etches the surface layer, thereby exposing a remaining layer of oxide to etching by the HF. Etching to the given thickness is difficult to control because the formation of  $\text{SiF}_4$  continues until the surface layer, i.e., the oxide layer, has been completely etched due to formation and evaporation of  $\text{SiF}_4$ .

[0029] According to Jeng et al., the reaction of HF with  $\text{SiO}_2$  when in contact with condensed ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ) is similar to the reaction in aqueous solution,  $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$ . However, instead of being released to the solution, the  $\text{SiF}_4$  product is trapped and reacts within the condensed film to produce  $(\text{NH}_4)_2\text{SiF}_6$ . The  $(\text{NH}_4)_2\text{SiF}_6$  is observed in IR spectra of reacted layers. Microbalance results also show the presence of the reacted layer. Condensation of  $\text{NH}_3$  and HF followed by desorption of the unreacted excess produces a frequency decline of 101 Hz, corresponding to reaction of 84 Å of the several thousand angstrom thick layer of  $\text{NH}_5\text{F}_2$  that initially condensed. After heating to 100°C there is a 103 Hz increase of resonant frequency corresponding to 58 Å of  $\text{SiO}_2$  being etched from the adapted surface layer of the silicon wafer.

[0030] Thermal desorption spectra are consistent with  $\text{SiF}_4$  released upon thermal decomposition of the reacted layer of ammonium hexafluorosilicate. The ammonium hexafluorosilicate layer can also be removed by rinsing in a solvent, such as water.

[0031] According to Jeng et al., the amount of  $\text{SiO}_2$  which may be etched may be controlled by providing a stoichiometric number of moles of HF to  $\text{NH}_3$  needed to form ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ), i.e. providing a molar ratio of HF to  $\text{NH}_3$  in the gas above the  $\text{SiO}_2$  surface substantially equivalent to 2. Pure HF etches  $\text{SiO}_2$  with no self-limiting process. Ammonia ( $\text{NH}_3$ ) is necessary to form the hexafluorosilicate product.

[0032] Jeng et al. discloses an apparatus and method in which ammonium bifluoride ( $\text{NH}_5\text{F}_2$ ) vapors can evaporate from an  $\text{NH}_5\text{F}_2$  effusion cell, leading to a non-stoichiometric  $\text{NH}_5\text{F}_2$  on the adapted surface layer being etched. An object of the present invention is to provide an apparatus and method in which the stoichiometric molar ratio of  $\text{HF}:\text{NH}_3 = 2$  needed to form  $\text{NH}_5\text{F}_2$  may be substantially uniformly and homogeneously provided on the adapted surface layer being etched.

[0033] In accordance with embodiments of the present invention, FIG. 1 depicts an exterior view of a single-substrate-processing non-plasma reaction apparatus 10, comprising an outer wall 8 of the apparatus 10, an exhaust port 83, dual manometers 85 and 87 and a lid 90. The outer wall 8 of the apparatus 10 may comprise a surface 91. The lid 90 comprises a surface 113 and a handle 95 on the surface 113. The apparatus 10 may further comprise a hinge 93, wherein a portion 89 of the hinge 93 may be coupled to the surface 91 of the outer wall 8, a portion 86 of the hinge 93 may be coupled to the surface 113 of the lid 90, and the portions 89 and 86 may be operatively coupled to a rotating portion 84 of the hinge 93. The rotating portion 84 of the hinge 93 may rotate on an axis parallel to the surface 91 of the wall 8 in a direction of an arrow 81. Referring to FIG. 1, the fluid feed line 99 passes through the lid 90 and extends to a source of first or second fluid (not shown) via a remaining portion of the fluid feed line 99 within the apparatus 10 as depicted in FIG. 2 and described infra. In a like manner, the fluid feed line 97 passes through the lid 90 and described herein and extends to a source of first or second fluid (not shown) via a remaining portion of the fluid feed line 97 within the apparatus 10 as depicted in FIG. 2 and described infra. The manometers 85 and 87 may be used to measure a pressure within the chamber 7 due in part to a flow of the first and second fluids through fluid feed lines 97 and 99. The manometer 85 may have a range from about 0-100 milli torr (mT) and the manometer 87 may have a range from about 0-100 torr. The first fluid may comprise, inter alia, ammonia ( $\text{NH}_3$ ) and the second fluid may comprise, inter alia, hydrogen fluoride (HF). The flow of  $\text{NH}_3$  may be provided to the fluid feed line 97 from about 3 to about 30 sccm at a pressure from about less than 1 psi to about 40 psi, and a flow of the HF may be provided to fluid feed line 99 from about 10 to about 60 sccm at a pressure from about less than 1 psi to about 5 psi. The fluid feed lines 97 and 99 may be alternatively provided with inter alia Argon or  $\text{N}_2$  gas.

[0034]

FIG. 2 depicts a top view of FIG. 1 after rotating the apparatus 10 in a counter-clockwise direction on a longitudinal axis through a center of the apparatus 10, such that the hinge 93 may be located at a top back position of the apparatus 10, and after lifting the lid 90 on the hinge 93 of the apparatus 10. Lifting the lid 90, wherein the rotating portion 84 of the hinge 93 was rotated 180 degrees in the direction of the arrow 81, exposed a portion 66 of a surface of the lid 90 that may be opposite and



parallel to the surface 113 of the lid 90, as depicted in FIG. 1 and described herein. The exposed surface 66 of the lid 90 may further comprise portions of the fluid feed lines 97 and 99 that may pass through the lid 90 as depicted in FIG. 1 and described herein. Referring to FIG. 2, a distribution plate 40 having an exposed surface 43 may be operatively coupled to the remaining portion (not shown) of a surface of the lid 90 that may be opposite and parallel to the surface 113 of the lid 90, as depicted in FIG. 1 and described herein. The distribution plate 40 may have been operably coupled to the lid 90 by inserting fasteners through holes 6.

[0035] The distribution plate 40 further comprises "I" rings, wherein I is a positive integer greater than or equal to 2, and wherein the rings have been denoted as  $R_X$  ( $X = 1, 2, \dots, I-1, I$ ). FIG. 2 shows rings 44, 46, 48, and 41, which are respectively denoted as  $R_1, R_2, R_{I-1}$ , and  $R_I$ . The rings  $R_X$  ( $X = 1, 2, \dots, I-1, I$ ) each have a common point P (i.e. point 49 in FIG. 2) on the surface 43 of the distribution plate 40, wherein P is within each  $R_X$  for values of  $X = 1, 2, \dots, I-1, I$ . Each ring  $R_X$  is totally within each ring  $R_{X+1}$  for values of  $X = 1, 2, \dots, (I-1)$ .

[0036] Additionally, each ring  $R_X$  has a perimeter of length  $D_X$ , ( $X = 1, 2, \dots, I-1, I$ ), such that  $D_1 < D_2 < \dots < D_I$ . Corresponding points in rings  $R_1, R_2, \dots, R_I$  are at increasing distance from the common point P. Each ring  $R_X$  ( $X = 1, 2, \dots, I$ ) has any geometrical shape such as inter alia, a circle, an ellipse, a rectangle or a square, etc.

[0037] Each ring of the I rings  $R_1, R_2, \dots, R_I$  in FIG. 2 comprises a distribution of channels 3 of a first type in which the first fluid may flow, or a distribution of channels 5 of a second type in which the second fluid may flow. There are  $n_1$  channels 3 of the first type in the I rings collectively, and there are  $n_2$  channels 5 of the second type in the I rings collectively. The first fluid from the fluid feed line 97 flows through the  $n_1$  channels 3 of the first type, and the second fluid from the fluid feed line 99 flows through the  $n_2$  channels 5 of the second type, as will be described infra in conjunction with FIG. 4. A ring that comprises channels 3 of the first type is called a ring of the first type, and a ring that comprises channels 5 of the second type is called a ring of the second type. There are  $I_1$  rings of the first type and  $I_2$  rings of the second type such that  $I_1 \geq 1, I_2 \geq 1$ , and  $I = I_1 + I_2$ . Thus the  $I_1$  rings of the first type collectively comprise the  $n_1$  channels 3 of the first type and no channels 5 of the

second type, and the  $l_2$  rings of the second type collectively comprise the  $n_2$  channels 5 of the second type and no channels 3 of the first type. For example, with  $l=4$  assumed, if  $l_1=2$  such that the  $l_1$  rings comprise rings  $R_1$  and  $R_3$  respectively having  $n_{11}$  and  $n_{13}$  channels 3 of the first type then  $n_1 = n_{11} + n_{13}$ , and if  $l_2=2$  such that the  $l_2$  rings comprise rings  $R_2$  and  $R_4$  respectively having  $n_{22}$  and  $n_{24}$  channels 5 of the second type, then  $n_2 = n_{22} + n_{24}$ . The first subscript "1" of  $n_{11}$  and  $n_{13}$  identifies the channels 3 of the first type and the first subscript "2" of  $n_{22}$  and  $n_{24}$  identifies the channels 5 of the second type. The second subscripts "1" and "3" of  $n_{11}$  and  $n_{13}$  identifies the channels 3 of the first type in the rings  $R_1$  and  $R_3$  respectively. The second subscripts "2" and "4" of  $n_{22}$  and  $n_{24}$  identifies the channels 5 of the second type in the rings  $R_2$  and  $R_4$ . Hereinafter, in the example with  $l=4$  assumed, if  $l_1=2$  such that the  $l_1$  rings comprise rings  $R_1$  and  $R_3$  respectively having  $n_{11}$  and  $n_{13}$  channels 3 of the first type and if  $l_2=2$  such that the  $l_2$  rings comprise rings  $R_2$  and  $R_4$  respectively having  $n_{22}$  and  $n_{24}$  channels 5 of the second type, then the rings  $R_1, R_2, R_3$  and  $R_4$  are "alternating rings." In a general case where  $l$  may be a positive integer greater than or equal to 2, assuming  $l_1 = l_2$  and  $l_1 + l_2 = l$ , a number of alternating rings having  $n_1$  channels of the first type or  $n_2$  channels of the second type is equal to  $l/2$ .

[0038]

The  $l_1$  rings of the first type and  $l_2$  rings of the second type may be arranged in any order with respect to the common point P. As a first example with  $l$  assumed to be even, the  $l_1$  rings of the first type and the  $l_2$  rings of the second type may alternate such that  $l_1 = l_2$ , wherein the  $l_1$  rings of the first type comprise rings  $R_1, R_3, \dots, R_{l_1-1}$ , and wherein the  $l_2$  rings of the second type comprise rings  $R_2, R_4, \dots, R_{l_2-1}$ . As a second example with  $l$  assumed to be odd, the  $l_1$  rings of the first type and the  $l_2$  rings of the second type may alternate such that  $l_1 = l_2 + 1$ , wherein the  $l_1$  rings of the first type comprise rings  $R_1, R_3, \dots, R_{l_1-1}$ , and wherein the  $l_2$  rings of the second type comprise  $R_2, R_4, \dots, R_{l_2-1}$ . As a third example with  $l$  assumed to be even, the  $l_1$  rings of the first type may exist in consecutive rings and the  $l_2$  rings of the second type may likewise exist in consecutive rings such that  $l_1 = l_2$ , wherein the  $l_1$  rings of the first type comprise rings  $R_1, R_2, \dots, R_{l_1/2}$ , and wherein the  $l_2$  rings of the second type  $R_{l_1/2+1}, R_{l_1/2+2}, \dots, R_{l_1}$ . As a fourth example with  $l$  assumed to be odd, the  $l_1$  rings of the first type may exist in consecutive rings and the  $l_2$  rings of

the second type may likewise exist in consecutive rings such that  $l_1 = l_2 + 1$ , wherein the  $l_1$  rings of the first type comprise rings  $R_1, R_2, \dots, R_{(l+1)/2}$ , and wherein the  $l_2$  rings of the second type comprise  $R_{(l+1)/2+1}, R_{(l+1)/2+2}, \dots, R_l$ . As a fifth example with  $l$  assumed to be odd, the  $l_1$  rings of the first type may exist in consecutive rings and the  $l_2$  rings of the second type may likewise exist in consecutive rings such that  $l_1 = l_2 - 1$ , wherein the  $l_1$  rings of the first type comprise rings  $R_1, R_2, \dots, R_{(l-1)/2}$ , and wherein the  $l_2$  rings of the second type comprise  $R_{(l-1)/2+1}, R_{(l-1)/2+2}, \dots, R_l$ .

[0039] Letting  $N_x$  denote the number of channels in ring  $R_x$  ( $x=1, 2, \dots, l$ ), the scope of the present invention comprises several special cases with respect to the number and distribution of channels in each ring. In a first special case,  $N_x$  increases monotonically as  $D_x$  increases. " $N_x$  increases monotonically as  $D_x$  increases" means  $N_x$  always increases as  $D_x$  increases. In a second special case,  $N_x$  increases about linearly as  $D_x$  increases. In some embodiments, for example,  $N_x$  is in a range of about 20 to about 72. In a third special case, the channels in each ring are approximately uniformly spaced apart. In some embodiments, a spacing between adjacent channels of uniformly spaced channels in a ring may be in a range of, inter alia, about 0.0875 inches to about 0.104 inches.

[0040] Referring to FIG. 2, lifting the lid 90, wherein the rotating portion 84 of the hinge 93 (see FIG. 1) was rotated 180 degrees in the direction of the arrow 81, also resulted in exposing a chamber 7 of the apparatus 10. The chamber 7 of the apparatus 10 further comprises a chamber wall 9 having an outer surface 12 and an inner surface 11. A portion 101 of the fluid feed line 97 may be located in the wall 9. The wall 9 may further comprise a portion 102 of the fluid feed line 99.

[0041] Referring to FIG. 2, the chamber 7 further comprises an upper annular ring 103 located such that a space or gap 107 exists between an edge 109 of the upper annular ring 103 and the inner surface 11 of the chamber wall 9. The upper annular ring 103 may be made from polytetrafluoroethylene or fluorinated ethylene propylene such as Teflon®, acetal homopolymer resin modified with DuPont™ Kevlar® resin such as Delrin®, polyimide materials such as Vespel® or Altymid®, polyetherimide materials such as Ultem®, polyarylate such as Ardel®, polycarbonate such as Lexan®, hard

coated aluminum, stainless steel and combinations thereof. The apparatus 10 further comprises an electrostatic chuck 110, wherein the electrostatic chuck 110 includes a feed line 117 for providing helium gas, grooves or glands 115 for distributing the helium gas, and holes 120 for wafer support pins. The electrostatic chuck 110 is called an electrostatic chuck because it electrostatically clamps onto a silicon wafer. The temperature of the wafer may be maintained from about  $-10^{\circ}\text{C}$  to about  $90^{\circ}\text{C}$ .

[0042] FIG. 3 depicts a top view of the electrostatic chuck 110 of FIG. 2, further comprising a surface or a sandwich 119 that may include a copper sheath sandwiched between an upper and lower layer of Kapton tape. Alternatively, the tape may be any polyimide tape. Applying a voltage from about 0 to about 2,000 volts DC to the surface or the sandwich 119 may result in coulomb attraction that may attract a wafer to the surface 119. The electrostatic chuck device may be obtained from Applied Materials, Inc., 3050 Bowers Avenue, Santa Clara, CA 95054-3299, U.S.A.

[0043] FIG. 4 depicts a cross-sectional view taken along line 4-4 of FIG. 1, wherein the apparatus 10 further comprises the distribution plate 40, operatively coupled to the lid 90, wherein the surface 43 of the distribution plate 40 faces away from the lid 90 and the surface 42 of the distribution plate 40 faces toward the lid 90. The distribution plate 40 may be operatively coupled to the lid 90 because the fluid feed line 97 has passed through the surface 113 as depicted in FIG. 1 and described herein, and has been operatively coupled to a cavity or groove 33 abutting the surface 42 of the distribution plate 40, and to the  $n_1$  channels 3 of the first type, as depicted in FIG. 2, and described herein. FIG. 4 further depicts the fluid feed line 99 after it has passed through the surface 113 as depicted in FIG. 2 and described herein, and has been operatively coupled to a cavity or groove 55 abutting the surface 42 of the distribution plate 40, and to the  $n_2$  channels 5 of the second type, as depicted in FIG. 2, and described herein. The fluid feed line 97 provides the first fluid to the cavity or groove 33 and the  $n_1$  channels 3 of the first type and the fluid feed line 99 provides the second fluid to the cavity or groove 55 and the  $n_2$  channels 5 of the second type.

[0044] The surface 42 of the distribution plate 40 may include a groove 121 between the channels 3 and 5, wherein the groove 121 may further comprise a bottom wall 54, and wherein a depth of the groove 121 from the surface 42 to the bottom wall 54 may

be at least 0.078 in. The groove 121 may include an o-ring or equivalent seal 123, wherein the seal 123 may prevent commingling of the first and second fluids in the  $n_1$  channels 3 of the first type and the  $n_2$  channels 5 of the second type respectively. An objective of the present invention is to have  $NH_3$  and HF, inter alia, enter chamber 7 without pre-mixing. O-rings or equivalent seals 123 are used as barriers to prevent the fluids in each ring  $R_X$  from mixing. The o-ring or equivalent seals 123 may be made from polytetrafluoroethylene or fluorinated ethylene propylene such as Teflon®, acetal homopolymer resin modified with DuPont™ Kevlar® resin such as Delrin®, polyimide materials such as Vespel® or Altymid®, polyetherimide materials such as Ultem®, polyarylate such as Ardel®, polycarbonate such as Lexan®, and combinations thereof. The first and second fluids may be sent to alternating rings (i.e., the first and second fluids may be sent to rings  $R_1, R_3, R_5, \dots$  and  $R_2, R_4, R_6, \dots$  respectively) so that as the first and second fluids respectively exit the channels 3 and 5 of each ring, there is no commingling of the first and second fluids until they enter the chamber 7 through the channels 3 and 5 of each ring.

[0045] The apparatus 10 further comprises a workpiece 30, wherein a portion 32 of the workpiece 30 has been adapted for being etched, and a remaining portion 31 has not been adapted. The workpiece 30 may comprise any semiconductor material such as silicon or germanium. The adapted surface layer 32 may be formed by oxidation of the silicon or germanium using any appropriate method of oxidation. For example, the adapted surface layer 32 of the workpiece 30 may be an oxide formed from tetraethoxysilane (TEOS) or alternatively from thermal oxidation. The workpiece 30 may be held in place by the electrostatic chuck 110.

[0046] A self-limiting etchable layer 50, having a surface 26, comprising ammonium hexafluorosilicate ( $(NH_4)_2 SiF_6$ ), has been formed from a portion of the adapted surface layer 32 of the workpiece 30, wherein a remaining portion 37 of the adapted surface 32 has become impervious to etching by the first or second fluid, such as hydrogen fluoride (HF), because the remaining portion 37 has been protected from the HF by the self-limiting layer 50, as disclosed by Jeng et al. in U.S. Patent 5,282,925, described herein.

[0047] A thickness of the self limiting layer 50 may be controlled, wherein a change of 1\*

in a temperature of the workpiece 30 equals a 17 Å etch rate change/minute, wherein the etch rate is directly proportional to the increase in temperature, in the temperature range from about -10 to about 90°C. A temperature controlling device 180 such as, for example, an aluminum cathode may be provided to maintain the temperature of the workpiece 30 within  $\pm 1^\circ\text{C}$  in the range from about -10 to about 90°C. The apparatus 10 further comprises a base flange 34 for supporting the temperature controlling device 180. The chamber wall 9 may also be provided with heating or cooling lines 104 to maintain the chamber wall 9 from about -10 to about 90°C.

[0048] Prior to forming the self-limiting etchable layer 50, the distribution plate 40 has been aligned over the adapted surface layer 32 of the workpiece 30. Hereinafter, "aligning the distribution plate 40" or "centering the distribution plate 40" or "the distribution plate 40 has been aligned" over the adapted surface layer 32 of the workpiece 30 means the center 163 of the cavity or groove 33, the center point 49 on the surface 43 of the distribution plate 40, the center 1 of the apparatus 10, and the center 165 of the workpiece 30 are located as points on a line 56, wherein the line 56 may be orthogonal to the surfaces 42 and 43 of the distribution plate 40 and the adapted surface layer 32 of the workpiece 30. The center 1 of the chamber 7 may be found at an intersection of transversal lines 57. The center 49 of the surface 43 of the distribution plate 40, and the center 26 of the workpiece 30 may be determined to be at an intersection of the respective transversal lines.

[0049] In addition to aligning the distribution plate 40 prior to forming the self-limiting etchable layer 50, the distribution plate 40 may be positioned a distance T from the adapted surface layer 32 of the workpiece 30. In an embodiment of the present invention, the distance T from the surface 26 of the adapted surface layer 32 of the workpiece 30 to the surface 43 of the distribution plate 40 includes from about 1/8 in. to about 3 1/2 in.

[0050] The chamber 7 of the apparatus 10 further comprises: the surface or sandwich 119 of the electrostatic chuck 110; the upper annular ring 103; the cathode insulator 105; and the lower annular ring 125, containing a plurality of exhaust holes 127 for distributing an exhaust flow provided by a vacuum pump, such as a turbo pump,

through the exhaust port 83. Referring to FIG. 4, in an embodiment of the present invention, an exhaust flow that originates from the exhaust port 83, as depicted in FIG. 1 and described herein, may be distributed through the plurality of exhaust holes 127 of the lower annular ring 125, resulting in a uniform or homogeneous atmosphere of reactive fluids over the workpiece 30 in the chamber 7. Hereinafter, "reactive fluids" include the first fluid, the second fluid, wherein the first or second fluids may be ammonia ( $\text{NH}_3$ ) or hydrogen fluoride (HF) and ammonium bifluoride ( $\text{NH}_4\text{F}_2$ ) and combinations thereof. Providing the reactive fluids over the adapted surface layer 32 of the workpiece 30, as a uniform or homogeneous atmosphere, forms the self-limiting etchable layer 50 that includes layers made of materials such as ammonium hexafluorosilicate ( $(\text{NH}_4)_2\text{SiF}_6$ ), that may become impervious to continued exposure to hydrogen fluoride (HF). Such imperviousness is the basis for the layer 50 being a self-limiting etchable layer. When the exhaust flow from the exhaust port 83 is distributed through the plurality of holes 127 in the lower annular ring 125, instead of through a single exhaust port, it was determined that a pressure of at least 4 torr may be provided without causing a concentration gradient of the fluids in the atmosphere, as may result if the lower annular ring 125 consisted of a single port, because the self-limiting etchable layer 50 had a uniform thickness. In another embodiment, providing the space or gap 107 between the upper annular ring 103 and the inner surface 11 of the chamber wall 9 restricted the exhaust flow from the exhaust port 83 and increased a concentration of the reactive fluids over the adapted surface layer 32, such that a change of  $1^\circ\text{C}$  equals a  $17 \text{ \AA}$  of etch rate change/minute, when the workpiece 30 was maintained at a temperature from about  $-10$  to about  $90^\circ\text{C}$ , and while operating at a pressure of at least 4 torr. In some embodiments, for example, the space or gap 107 may be a distance from the edge 109 of the upper annular ring 103 to the inner surface 11 of the chamber wall 9 and may be at least  $3/8$  in. Referring to FIGS. 3 and 4, the workpiece 30 may be supported by lift pins that may be inserted through holes 120 of the surface 119 of the electrostatic chuck 110. The distribution plate 40, the o-rings 123, the upper annular ring 103, the cathode insulator 105 and lower annular ring 125 may be made from polytetrafluoroethylene or fluorinated ethylene propylene such as Teflon®, acetal homopolymer resin modified with DuPont™ Kevlar® resin such as Delrin®, polyimide materials such as Vespel® or Altyimid®, polyetherimide materials such as Ultem®,